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Environmental economics of lignin derived transport fuels



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Biochemical based cellulosic biorefineries with ethanol production capacities

TECHNOLOGY

| Year | Ligno (Kilowatt) | Process | DuPont | POET (POET-DIM) | Inbicon (MTC) | Abengoa |
|------|----------------------------------|---|-------------------------------|-------------------------------|---|---------|
| 2008 | Ligno 1 (Canada) | POET 1 (Canada, U.S.) U.S.: 100 M\$/year | | | Abengoa / Marana, U.S. U.S.: 50 M/year | |
| 2010 | Biochemtech / Italy | DuPont / Tennessee U.S.: 0.95 M\$/year | | | Abengoa / Spain 3 M\$/year | |
| 2012 | Ligno 2 (Canada) 2.1 M\$/year | | | | | |
| 2014 | Chemistry / Italy 70 M\$/year | | | | | |
| 2016 | POET 2 (U.S.) 412 M\$/year | POET 3 (U.S.) 412 M\$/year | POET 4 (U.S.) 412 M\$/year | POET 5 (U.S.) 412 M\$/year | Abengoa / Marana, U.S. 54.6 M\$/year | |
| 2018 | POET 6 (U.S.) 118.8 M\$/year | DuPont / U.S. 118.8 M\$/year | | | | |
| 2019 | POET 7 (U.S.) 118.8 M\$/year | | | | | |
| 2020 | POET 8 (U.S.) 118.8 M\$/year | | | | | |
| 2021 | POET 9 (U.S.) 118.8 M\$/year | | | | | |
| 2022 | POET 10 (U.S.) 118.8 M\$/year | | | | | |
| 2023 | POET 11 (U.S.) 118.8 M\$/year | | | | | |
| 2024 | POET 12 (U.S.) 118.8 M\$/year | | | | | |
| 2025 | POET 13 (U.S.) 118.8 M\$/year | | | | | |
| 2026 | POET 14 (U.S.) 118.8 M\$/year | | | | | |
| 2027 | POET 15 (U.S.) 118.8 M\$/year | | | | | |
| 2028 | POET 16 (U.S.) 118.8 M\$/year | | | | | |
| 2029 | POET 17 (U.S.) 118.8 M\$/year | | | | | |
| 2030 | POET 18 (U.S.) 118.8 M\$/year | | | | | |
| 2031 | POET 19 (U.S.) 118.8 M\$/year | | | | | |
| 2032 | POET 20 (U.S.) 118.8 M\$/year | | | | | |
| 2033 | POET 21 (U.S.) 118.8 M\$/year | | | | | |
| 2034 | POET 22 (U.S.) 118.8 M\$/year | | | | | |
| 2035 | POET 23 (U.S.) 118.8 M\$/year | | | | | |
| 2036 | POET 24 (U.S.) 118.8 M\$/year | | | | | |
| 2037 | POET 25 (U.S.) 118.8 M\$/year | | | | | |
| 2038 | POET 26 (U.S.) 118.8 M\$/year | | | | | |
| 2039 | POET 27 (U.S.) 118.8 M\$/year | | | | | |
| 2040 | POET 28 (U.S.) 118.8 M\$/year | | | | | |
| 2041 | POET 29 (U.S.) 118.8 M\$/year | | | | | |
| 2042 | POET 30 (U.S.) 118.8 M\$/year | | | | | |
| 2043 | POET 31 (U.S.) 118.8 M\$/year | | | | | |
| 2044 | POET 32 (U.S.) 118.8 M\$/year | | | | | |
| 2045 | POET 33 (U.S.) 118.8 M\$/year | | | | | |
| 2046 | POET 34 (U.S.) 118.8 M\$/year | | | | | |
| 2047 | POET 35 (U.S.) 118.8 M\$/year | | | | | |
| 2048 | POET 36 (U.S.) 118.8 M\$/year | | | | | |
| 2049 | POET 37 (U.S.) 118.8 M\$/year | | | | | |
| 2050 | POET 38 (U.S.) 118.8 M\$/year | | | | | |
| 2051 | POET 39 (U.S.) 118.8 M\$/year | | | | | |
| 2052 | POET 40 (U.S.) 118.8 M\$/year | | | | | |
| 2053 | POET 41 (U.S.) 118.8 M\$/year | | | | | |
| 2054 | POET 42 (U.S.) 118.8 M\$/year | | | | | |
| 2055 | POET 43 (U.S.) 118.8 M\$/year | | | | | |
| 2056 | POET 44 (U.S.) 118.8 M\$/year | | | | | |
| 2057 | POET 45 (U.S.) 118.8 M\$/year | | | | | |
| 2058 | POET 46 (U.S.) 118.8 M\$/year | | | | | |
| 2059 | POET 47 (U.S.) 118.8 M\$/year | | | | | |
| 2060 | POET 48 (U.S.) 118.8 M\$/year | | | | | |
| 2061 | POET 49 (U.S.) 118.8 M\$/year | | | | | |
| 2062 | POET 50 (U.S.) 118.8 M\$/year | | | | | |
| 2063 | POET 51 (U.S.) 118.8 M\$/year | | | | | |
| 2064 | POET 52 (U.S.) 118.8 M\$/year | | | | | |
| 2065 | POET 53 (U.S.) 118.8 M\$/year | | | | | |
| 2066 | POET 54 (U.S.) 118.8 M\$/year | | | | | |
| 2067 | POET 55 (U.S.) 118.8 M\$/year | | | | | |
| 2068 | PO | | | | | |

Life cycle assessment

This paper explores the environmental and economic aspects of fast pyrolytic conversion of lignin, obtained from 2G ethanol plants, to transport fuels for both the marine and automotive markets. Various scenarios are explored, pertaining to aggregation of lignin from several sites, alternative energy carriers to replace lignin, transport modalities, and allocation methodology. The results highlight two critical factors that ultimately determine the economic and/or environmental fuel viability. The first factor, the logistics scheme, exhibited the disadvantage of the centralized approach, owing to prohibitively expensive transportation costs of the low energy-dense lignin. Life cycle analysis (LCA) displayed the second critical factor related to alternative energy carrier selection. Natural gas (NG) chosen over additional biomass boosts well-to-wheel greenhouse gas emissions (WTW GHG) to a level incompatible with the reduction targets set by the U.S. renewable fuel standard (RFS). Adversely, the process' economics revealed higher profits vs. fossil energy carrier.

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Numerous studies have reported significant environmental benefits of 2G relative to 1G ethanol production (Sims et al., 2010; Dias et al., 2011; Menten et al., 2013). Nevertheless, while the former is slightly cheaper than petrol, the latter is more pre-

ferred than both (Peplow, 2014). It is therefore worthwhile to investigate the environmental and economic aspects of converting lignin, a major 2G ethanol plant discharge now burnt onsite for steam-electricity, into higher value products, including biofuels (PNNL, 2007; Zakzeski et al., 2010; Boot, 2016). Unfortunately, the immaturity of most conversion technologies, a deficiency further exacerbated by a lack of data on environmental economics, only strengthens the dogma that lignin valorization is a dead end (PNNL, 2007; Azadi et al., 2013).

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This paper sets out to persistently summarize the literature on lignin (e.g., ex 2G ethanol plant) conversion to transport fuels and evaluate the implied environmental economics. To this end, we first discuss the techno-economic feasibility of fast pyrolysis, arguably the most proven technology to produce fuels from solid biomass, as the lignin conversion process of choice. Two fuels will be considered as end products here, the raw pyrolysis oil and the hydro-treated upgraded version thereof. Former and latter fuels servicing the low sulfur heavy marine fuel and automotive diesel markets, respectively.

In the second part of this paper, a life cycle assessment (LCA) will be presented with respect to greenhouse gas (GHG) emissions of aforementioned lignin-derived biofuels. The overall goal of this paper is to assess whether or not it is economically and/or environmentally feasible to produce transport fuels from lignin obtained from 2G ethanol plants.

2. Methodology

2.1. Process description – fast pyrolysis

Pyrolysis refers to the thermal destruction of biomass in the absence of oxygen, which results in three outputs in more or less equivalent ratios: oil, char and gas. While low temperature and a longer vapor treatment time facilitate the production of char, a higher temperature range increases gas yield (Bridgwater, 2012). Fast pyrolysis, that implies moderate temperatures of about 500 °C and a short vapor residence time of less than 2 s, provides better conditions for bio-oil production, mainly due to avoiding undesirable secondary reaction, as well as tar coking (Bridgwater, 2012). Oil alone is considered as a feedstock for subsequent transport fuel production, with the other co-products typically being burnt on site for steam-electricity (PNNL, 2009; Wright et al., 2010; Trinh et al., 2013a).

Lignin is a complex polymer, for the greater part comprising three derivatives of coumaryl, coniferyl and sinapyl alcohols. These are p-hydroxyphenyl-, guaiacyl- and syringyl-, or H-, G- and S-units, respectively (Zakzeski et al., 2010; Jong and Gosselink, 2014). Lignin content in biomass may vary from 15% in switchgrasses to 50% in drupes (Zakzeski et al., 2010; Mendu et al., 2011). On average, lignin is responsible for roughly 40% of the calorific value of lignocellulosic biomass (PNNL, 2007; Zakzeski et al., 2010).

However, given specific lignin structure its pyrolysis differs from that of biomass, generally resulting in lower bio-oil yields compared to one where biomass is used as a primary feedstock (Trinh et al., 2013a; Wright et al., 2010; Lv et al., 2013).

Altogether, pyrolysis temperature, vapor residence time and the type of lignin used can affect both yield and oil composition. The highest oil yield is found for temperatures ranging from 500–600 °C, 43 wt% on dry basis (Trinh et al., 2013a) and 44.89 wt% (Lv et al., 2013), though Jones and Zhu assumed it varying from 31% to 53% for high and low char case, respectively (PNNL, 2009). Maximum output of phenolic compounds in the oil is observed at around 550–600 °C (Lv et al., 2013; Trinh et al., 2013a; Lou et al., 2015). Oils produced at temperatures below 500 °C tend to be unstable, having a pronounced tendency to re-polymerize (Lou et al., 2015; Bai et al., 2014). For temperatures in excess of 550 °C, secondary reactions, resulting in increase of the gas yield, start to play a material role (Trinh et al., 2013a).

Pyrolysis of lignin obtained from herbaceous biomass, including corn stalk, yields higher amounts of H-phenols as the temperature rises from 400–900 °C. The output of G-phenols, however, peaks at around 500–550 °C (Lv et al., 2013; Trinh et al., 2013a). H-phenols were found to be the major compounds of lignin pyrolysis oil orig-

inating from corn stover at 500 °C (Patwardhan et al., 2011), while the major compounds identified in oil produced from switchgrass (650 °C, 20 s) and wheat straw (550 °C, 0.8 s) were G-type phenols (Mendu et al., 2011; Trinh et al., 2013a). In general, pyrolysis oil of lignin derived from herbaceous biomass contains only trace amounts of S-phenols.

Fast pyrolysis of softwood lignin at 500 °C and 600 °C resulted in G-phenols being amongst the most prevalent oil constituents (Faix et al., 1987; Kuroda and Nakagawa-izumi, 2006). As for the pyrolysis of hardwood lignin (e.g., beech), the output of S-phenols was twice that found for G-phenols, with negligible H-phenols yields (Faix et al., 1987).

An important limitation of this study is that the analysis of pyrolysis oil concerns oil produced from technical lignins, rather than actual industrial 2G ethanol plant lignin residue. The latter stream contains, in addition to lignin, up to 25 ÷ 35 wt-% of residual sugars and 10 ÷ 15 wt-% of ashes (Palmisano, 2013). The impact of these impurities on oil yields and fuel quality is not taken into account here.

2.2. Transport fuels

2.2.1. Automotive

The benefits of the oxygenated aromatic structure typical of lignin-derived biofuels are outlined in several studies (Zhou et al., 2013, 2014; Boot, 2016). The combined presence of oxygen and unsaturated bonds inherently suppresses the gravimetric heating value (e.g., 29.7 MJ/kg for lignin pyrolysis oil (Trinh et al., 2013b) vs. 42.2 MJ/kg for residual fuel oil). However, owing to the intrinsically high densities of oxygenated aromatics as class, a neutral to even positive impact on volumetric calorific value can be expected when switching from fossil fuels to lignin derived oxygenated aromatics (Zhou et al., 2014).

As is the case for the gravimetric heating value, fuel oxygen and unsaturated bonds generally have a negative impact on the cetane number, a measure of diesel quality. Accordingly, for road going diesel applications, lignin pyrolysis oil has to be processed further via hydro-deoxygenation in order to saturate the carbon bonds and eliminate the oxygen groups.

2.2.2. Marine

Understandably, this upgrading procedure is quite capital and energy intensity, hurting, as will be demonstrated later, the overall environmental economic viability of the business case. It is for this reason that a second fuel application is considered, namely low sulfur heavy marine fuel oil. Interestingly, energy density and cetane number are not the key metrics for fuel value in this sector. Rather, costs per GJ are the decisive factor here. Moreover, water and high viscosity are typically not major issues either.

Accordingly, it will be assumed in the further analysis that unprocessed lignin pyrolysis oil can already be sold as a substitute heavy fuel oil (HFO) for large two stroke marine engines. As lignin from 2G ethanol plants contains only negligible amounts of sulfur, the price benchmark is not highly sulfurous HFO, but the considerably more expensive and low sulfur marine gas oil (LSMGO). Given the stringent sulfur legislation in many seas and coastal zones these days, the latter, higher quality fuel must now be bunkered in lieu of the lower grade variant when sailing in so-called sulfur emission control areas (SECA's).

2.3. Feedstock availability

Among the industrial processes allowing the production of lignin, the sulphate or Kraft cooking process is by far the most prevalent route, accounting for roughly 85% of total lignin production (Chen, 2015). A drawback of this process, particularly when target-

Table 1
Biochemical based commercial-scale cellulosic biorefineries.

| Project and start of operation | Ethanol capacity, ML/year | Primary feedstock | | | Pre-treatment | Lignin residue | | Lignin Dis-placement | References |
|---|---------------------------|--|-------------------------|-------------------|---|---|---|----------------------|--------------------------------------|
| | | Type | Mass, million t/ year | Supply radius, km | | Amount, DT/ year | Utilization | | |
| <i>Operating</i> | | | | | | | | | |
| Crescentino Bio-refinery/ Italy/2013 | 76 | Energy grasses, wheat straw | 0.27 | 70 | Steam explosion (Proesa™ tech) | 185,000 with lignin fraction of 45 ÷ 60% (estimated) | 13 MW combined heat and power (CHP) plant, excess of electricity is supplied to the grid | No data | Chiaromonti (2013), Palmisano (2013) |
| Project Liberty (POET-DSM)/ Iowa, U.S./ 2014 | 94.6 | Corn stover (CS) | 0.34 | 56 | Dilute sulphuric acid/Steam | 104,790 (estimated) | 37 MW solid fuel boiler fed by lignin, corn cobs and sludge from waste water treatment (WWT). Steam is used for 2G ethanol process | Natural gas (NG) | ENSR/AECOM (2008) |
| Abengoa Bio-refinery Project/ Kansas, U.S./ 2014 | 94.6 | CS, wheat straw, milo stubble, mixed warm season grasses | 0.33 (on dry basis) | 80 | Dilute sulfuric acid/Steam | 90,718 | CHP plant fed by lignin, syrup from distillation and sludge from WWT. Gross electricity generation capacity: 20 MW. Steam and electricity are used for 2G ethanol process | NG, coal | USDOE (2010) |
| Bioflex 1 plant (GranBio)/ Brazil/2014 | 82 | Sugarcane straw | 0.35 | 20 | Steam explosion (Proesa™ tech) | 200,000 (estimated) | CHP plant fed by lignin residue and bagasse. Steam and electricity are used for 2G ethanol process. Electricity, 135 GWh/year, is exported to the grid. | No data | Gonçalves et al. (2015) |
| Raizen – expansion of sugar cane mill Costa Pinto/Brazil/ 2014 | 42.2 | Sugarcane straw | No data | No data | Mild acid hydrolysis (sulfuric acid)/Steam explosion (logen tech) | No data | Boiler is fed by lignin and bagasse. | No data | USDA (2015) |
| DuPont cellulosic bio-refinery/ Iowa, U.S./ 2015 | 113.6 | CS | 0.375 (on dry basis) | 48 | Ammonia/ Steam | 82,335 (estimated) | Boiler is fed by lignin and syrup. Lignin is also considered as marketable product. | No data | DuPont (2014a) |
| <i>Announced for start-up in near future</i> | | | | | | | | | |
| Fuyang Bioproject/ China/2016 | 250 | Wheat straw and CS | 1 | No data | Steam explosion (Proesa™ tech) | 610,000 | Boilers (2 × 130t/h, 30 MW) are fired by lignin residue with further steam utilization at a 45 MW CHP plant. | No data | Biochemtex (n.d.) |
| Strazske bio-refinery/ Slovakia/ 2017 | 70 | Wheat straw | No data | No data | Steam explosion (Proesa™ tech) | 170,000 (estimated) | CHP plant. Steam and electricity are used for the bio-refinery needs. Electricity excess is sold to the grid. | No data | Beta Renewables (n.d.) |
| Maabjerg Bioethanol (part of Maabjerg Energy Concept)/ Denmark/ 2018 | 77 | Straw | 0.3 | 100 | Steam explosion (Inbicon tech) | 83,636 with moisture of 10% | Production of lignin pellets. CHP plant fed by lignin from bio-refinery, biogas and fiber from biogas plant. Steam and electricity are used for 2 G ethanol process and for external purposes | Waste, coal | MEC (2015) |
| DuPont cellulosic bio-refinery/ Macedonia/ 2018 | 100 | Non-food biomass | No data | No data | Ammonia/ Steam | 72,478 (estimated) | No data | No data | DuPont (2014b) |
| Project Alpha/ North Carolina, U. S./2018 | 75 | Energy grasses | 0.15 ÷ 0.4 on dry basis | 50 | Steam explosion (Proesa™ tech) | 57,144 high purity chemical grade lignin (assuming 5% moisture content) | On-site boiler for steam production. Steam is used for 2G ethanol process | Biogas, NG | USDA (2011) |
| BlueFire Fulton cellulose bio-refinery/ Mississippi, U.S./start of operation is unknown | 70 | Woody biomass, agricultural residue, cellulosic MSW | 0.43 | 120 | Arkenol concentrated acid hydrolysis process | 173,800 with lignin fraction of 30% | On-site boiler for steam production. Steam is used for 2G ethanol process | NG | AECOM Environment (2010) |

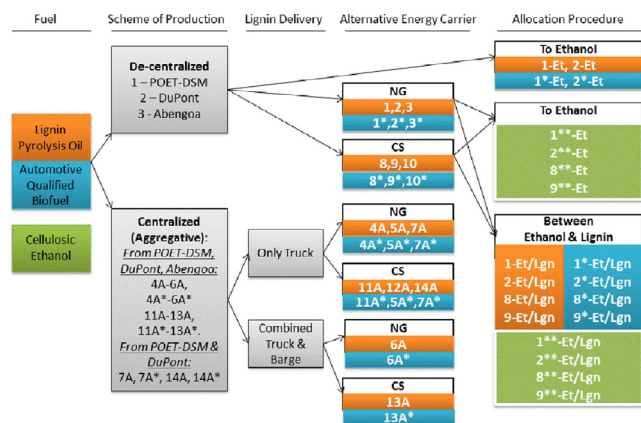


Fig. 1. Investigated scenarios (NG – natural gas; CS – corn stover; Et – Ethanol; Lgn – lignin).

ing transport fuels as end products, is the high sulfur content, which ranges from 2 to as high as 3 wt-% of (Sjostrom, 2013). Alternatively, sulfide pulping, yields so-called lignosulfonates as effluent (Calvo-Flores et al., 2015). These lignin compounds are already being commercially deployed as a low-cost additive in concrete, clay and other materials (Northey, 2002).

More recently, sulfur free lignin is being produced by cellulosic ethanol plants that involve several steps of lignocellulosic biomass treatment: first, pretreatment of the biomass, which is usually aimed to separate lignin, followed by hydrolysis converting cellulose and hemicellulose to monomeric sugars (hexoses), and then by the subsequent fermentation stage, which includes the transformation of sugars to ethanol with the use of yeast (Verardi et al., 2012).

The pretreatment techniques, besides the mechanical treatment of lignocellulosic biomass, can comprise physio-chemical methods (e.g. steam pretreatment, ammonia-fiber explosion method, or other), or chemical methods, e.g. dilute acid or alkaline hydrolysis. Quite often, the pretreatment step, apart from the separation of the lignin layer, alters the lignin structure as well (Verardi et al., 2012).

As of 2016, there were 7 operational commercial-scale cellulosic ethanol plants worldwide, with another 6 planned for the near future (Table 1). Cumulatively, these plants are set to produce over 1600 kton of sulfur-free lignin (dry basis) by 2018. The dominant 2G ethanol process at this time is arguably the Proesa technology developed by Beta Renewables, an Italian producer of biofuels and biochemicals from agricultural residues and non-food plants. Proesa is based on steam explosion and subsequent enzymatic hydrolysis of agricultural residues.

As can be derived from Table 1, agricultural wastes and energy crops are the most widely used lignocellulosic feedstocks. Indeed, 2G ethanol plants by Beta Renewables, POET-DSM (Project Liberty), Abengoa, DuPont, Raizen (Iogen), Inbicon are fed solely by such herbaceous biomass. From the data available, it would appear that BlueFire (Fulton) alone relies on woody biomass (AECOM Environment, 2010). The maximal capacity of 2G ethanol plants is limited mainly by the amount of biomass that can be reasonably harvested within a 50–100 km radius (Kudakasseril Kurian et al., 2013).

2.4. Alternative energy carriers

Most 2G ethanol plants are designed to be self-sufficient in their steam-electricity needs. To this end, residual lignin, biogas and, when necessary, additional biomass typically serve as energy carriers. In fact, only two plants of those reviewed in Table 1 import electricity, namely BlueFire Fulton and Project Liberty. The latter plant utilizes the concept of an integrated bio-refinery, supplying biogas to an adjacent grain-to-ethanol, or 1G ethanol facility. Accordingly, in most cases, the conversion of lignin into the higher value products automatically implies that a substitute energy carrier be imported.

Among the alternatives under consideration are natural gas (NG), coal, agricultural waste (e.g., Maabjerg BioEnergy) or even the lignocellulosic feedstock in question (Table 1). From an economical stance, the replacement of lignin by NG could improve the bottom line, given that a gas-fired boiler is generally considered to be a more cost-effective – and water saving – route to

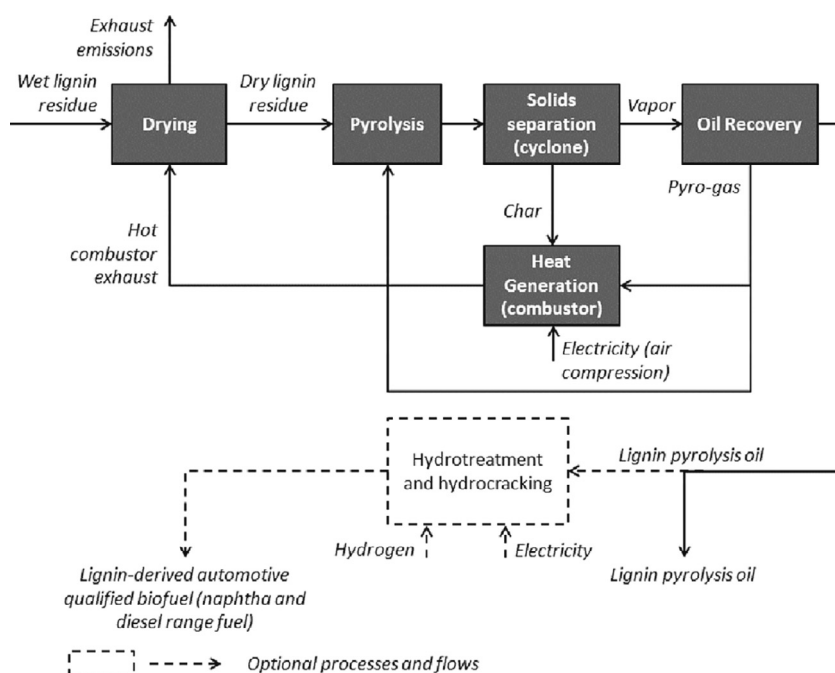


Fig. 2. Scheme of lignin fast pyrolysis with optional hydroprocessing stage.

Table 2

Input data used for the techno-economic and LCA models.

| Parameter | Unit | Value |
|--|--------------------------------------|------------------------------------|
| <i>Techno-economic model</i> | | |
| <i>Truck Mode</i> | | |
| Truck lifetime | Years | 6 |
| Truck capital cost for lignin and for biofuel delivery | \$ | 146,920 |
| Truck O&M cost | % of capital | 15 |
| Insurance | % of capital/year | 3 |
| Fuel consumption | L/km | 0.4 |
| Fuel price | \$/L | 0.97 |
| Winding road factor | – | $\sqrt{2}$ |
| Number of working days per year | Days/year | 251 |
| Number of working hours per day | h/day | 24 |
| Driver earning | \$/h | 12 |
| Payload | t/truck | 26 |
| Non-driving roundtrip time for lignin delivery | h/round trip | 1.2 |
| Non-driving roundtrip time for biofuel delivery | h/round trip | 1.1 |
| Truck average speed | km/h | 75 |
| <i>Barge Mode</i> | | |
| Barge load | t/barge | 1500 |
| Number of barges in tow | – | 15 |
| Barge average speed | km/day | 161 |
| Cost of cargo shipment (for trip duration of 11 days) | \$/t | 8.5 |
| <i>Pyrolysis plant and hydroprocessing</i> | | |
| Project lifetime | years | 25 |
| Pyrolysis oil – yield (dry basis) | % | 33 |
| Pyrolysis oil – water content (on wet basis) | % | 28.7 |
| Automotive qualified fuel – yield from pyrolysis oil | % | 42 |
| Installed cost of hydroprocessing equipment | Million \$ for processing of 1 t/day | 0.007 |
| Plant O&M cost, including hydrotreatment and hydrocracking equipment (for the scenarios with hydroprocessing) | % of capital/year | 2 |
| Insurance and taxation | % of capital/year | 1.5 |
| Power consumed by pyrolysis plant | kWh/DT of lignin | 68 |
| Specific electricity consumption in hydroprocessing stage | kWh/DT of hydro-processed biofuel | 549.6 |
| Specific hydrogen consumption in hydroprocessing stage | MJ/DT of hydro-processed biofuel | 10,360.7 |
| Catalyst replacement cost | \$/year per 1 t of initial CS | 2.7 |
| <i>Lignin storage</i> | | |
| Project lifetime | years | 25 |
| Investment cost per square meter | \$/m ² | 125.4 |
| Storage O&M cost | % of capital/year | 4 |
| Storage facility height | m | 6 |
| Wet lignin density | t/m ³ | 1.185 |
| Loss coefficient | %/year | 6 |
| <i>Raw materials, energy carriers and interest rate</i> | | |
| Lignin stillage price, assuming that lignin is displaced by natural gas with price of 2.8 \$/GJ | \$/DT | 62 |
| Lignin stillage price, assuming that lignin is displaced by corn stover with total price of 73 \$/DT of corn stover, including purchase and handling costs | \$/DT | 94 |
| Electricity price | \$/kWh | 0.066 |
| Hydrogen purchase price | \$/kg | 1.65 |
| Interest rate | % | 7 |
| <i>LCA model</i> | | |
| <i>CS harvesting, collection and transportation</i> | | |
| Supplemental N fertilizer | g/DT of CS | 8488 |
| Supplemental P fertilizer | g/DT of CS | 2205 |
| Supplemental K fertilizer | g/DT of CS | 13228 |
| Transportation distance for bio-refinery of type 1 | km | 56.3 |
| Transportation distance for bio-refinery of type 2 | km | 48 |
| <i>Cellulosic bio-refinery</i> | | |
| CS consumption rate (bio-refinery of type 1) | DT/liter of ethanol | 0.0036 |
| CS consumption rate (bio-refinery of type 2) | DT/liter of ethanol | 0.0028 |
| Fuel fed to the boiler (bio-refinery of type 1): | DT/liter of ethanol | 0.000910.001077.7*10 ⁻⁵ |
| Corn cobs | | |
| Lignin rich stillage cake | | |
| Sludge | | |
| Fuel fed to the boiler (bio-refinery of type 2): | DT/ liter of ethanol | 0.00120.00076 |
| Corn cobs | | |
| Lignin rich stillage cake | | |
| Electricity consumption: | kWh/ liter of ethanol | 1.081.03 |
| bio-refinery of type 1 | | |
| bio-refinery of type 2 | | |

(continued on next page)

Table 2 (continued)

| Parameter | Unit | Value |
|--|-----------------------|----------|
| Electricity sold (bio-refinery of type 2) | kWh/ liter of ethanol | 0.54 |
| Process chemicals (bio-refinery of type 1): | | |
| Sulfur acid | kg/l | 0.091 |
| Ammonia | kg/l | 0.011 |
| Yeast | g/l | 7.46 |
| Enzymes | kg/l | 0.030 |
| Corn steep liquor | g/l | 35 |
| Sodium hydroxide | g/l | 31 |
| Urea | g/l | 5.5 |
| Calcium oxide | g/l | 20 |
| Process chemicals (bio-refinery of type 2): | | |
| Sulfur acid | kg/l | 0.066 |
| Ammonia | kg/l | 0.038 |
| Yeast | g/l | 7.46 |
| Enzymes | kg/l | 0.030 |
| <i>Lignin pyrolysis oil production</i> | | |
| Lignin consumption rate | DT/DT of oil | 3.02 |
| Bio-char consumption rate | t/DT of oil | 1.81 |
| Pyro-gas consumption rate | t/DT of oil | 0.23 |
| Electricity consumption | kWh/DT of lignin | 68 |
| <i>Hydroprocessing</i> | | |
| Biofuel yield | % | 42 |
| Hydrogen consumption | MJ/ DT of biofuel | 10,360.7 |
| Electricity consumption | kWh/DT of biofuel | 549.6 |
| <i>Biofuel distribution</i> | | |
| Ethanol: | | |
| heavy-duty tracks | km | 145 |
| rail | km | 2881 |
| Lignin pyrolysis oil and automotive qualified biofuel (heavy-duty tracks): | | |
| bio-refinery of type 1 | km | 336 |
| bio-refinery of type 2 | km | 235 |

Comment to the table: bio-refinery of type 1 – bio-refinery with consumption of electricity from the grid; bio-refinery of type 2 – bio-refinery with electricity production on-site.

steam-electricity (Scown et al., 2014). However, NG, contrary aforementioned lignocellulosic energy carriers, is a fossil fuel and as such is both non-renewable as well as more GHG intensive. Alternatively, bio-refineries can opt to consume some part of their biomass input for steam-electricity production. Setting aside economic implications for a moment, the concept of substituting lignin by additional biomass is a sound solution when the overall goal is to minimize GHG emissions.

2.5. Modelling

As stated earlier, this paper investigates the environmental economics of two lignin derived transport fuels, crude pyrolysis oil and the hydroprocessed version thereof. Former and latter fuels will be benchmarked against low sulfur marine gas oil and ultra-low sulfur diesel fuel, respectively. The analysis comprises techno-economic modelling and GHG emissions focused life cycle assessment (LCA).

2.5.1. Scenarios

Three constructed U.S. based 2G ethanol plants, Project Liberty (POET-DSM), DuPont and Abengoa, will serve as case studies here, for which various scenarios will be explored (Fig. 1). LCA modelling will be confined to the most promising cases found in the foregoing economic analysis.

2.5.2. Techno-economic model

The techno-economic model is based on the minimization of net present cost (NPC), which takes into account both capital

(CAPEX) and operational (OPEX) expenditure, discounted using annual interest rate (r) over the project lifetime (R):

$$NPC = \frac{C_{ann}}{CRF(r, R)}, [\text{\$}] \quad (1)$$

where the capital recovery factor (CRF) is a function of R and r :

$$CRF = \frac{r \times (1 + r)^{R_{proj}}}{(1 + r)^{R_{proj}} - 1} \quad (2)$$

The annualized cost (C_{ann}) have been defined as the sum of related annualized capital and replacement costs, yearly O&M, cost of fuel, electricity, hydrogen purchase, replacement of catalyst, insurance, driver wages, etc. Annualized capital cost of trucks and plant have been calculated via application of the CRF function to capital investment.

Regarding the comparison of production costs for different types of biofuels, it is more reasonable to parallel them based on fuel energy content. The latter can be obtained from NPC using the following equation:

$$P_{fuel} = \frac{NPC \cdot CRF}{m_{fuel} \cdot LHV_{fuel}}, [\text{\$/GJ}] \quad (3)$$

The pyrolysis model is based on results obtained from (PNNL, 2009; Rogers and Brammer, 2012), whereby dried lignin residue undergoes fast pyrolysis at the temperature of 499 °C and a residence time shorter than 1 s (Fig. 2). Combustion products and non-condensable pyrolysis gases serve to provide heat for the drying process and maintain the requisite thermal conditions in the reactor.

The basis for the plant sizing curve is in accordance with the procedure as outlined in (Rogers and Brammer, 2012), which describes such a curve for a biomass-to-bio-oil pyrolysis facility. The curve is further expanded here to take into account the pre-treatment phase of lignin residue, which includes extensive drying:

$$C_{PlantCap} = (2853.8 \cdot \ln(x) - 6958.8) \cdot 2029.5, [\$/] \quad (4)$$

where $C_{PlantCap}$ denotes the plant capital investment, x is daily plant capacity in lignin pyrolysis oil dry tons. Eq. (4) includes the inflation coefficient, normalizing costs to the year 2015.

Electricity used by a pyrolysis plant ($C_{PlantEl}$) is mainly required for gas compression (Rogers and Brammer, 2012; Braimakis et al., 2014). Given this, the annual cost of electricity is defined via power consumed by the pyrolysis process (P_{compr}), amount of treated lignin (m_{Lignin}) and electricity price (P_{El}):

$$C_{PlantEl} = P_{compr} \cdot m_{Lignin} \cdot P_{El}, [\$/year] \quad (5)$$

The cost of electricity ($C_{HydroprocessingEl}$) and hydrogen ($C_{Hydrogen}$) required for hydroprocessing stage are a function of the amount of obtained biofuel ($m_{Biofuel}$), electricity and hydrogen consumption in hydroprocessing stage ($S_{Hydroprocessing}$ and $S_{Hydrogen}$), hydrogen purchase price ($P_{Hydrogen}$) and electricity price:

$$C_{HydroprocessingEl} = m_{Biofuel} \cdot S_{Hydroprocessing} \cdot P_{El}, [\$/year] \quad (6)$$

$$C_{Hydrogen} = m_{Biofuel} \cdot S_{Hydrogen} \cdot P_{Hydrogen}, [\$/year] \quad (7)$$

The truck transport model and its design parameters are based on (Gonzales et al., 2013; Braimakis et al., 2014).

Transportation by barge implies only the service payment:

$$C_{annBarge} = P_{Barge} \cdot m_{cargo} [\$/year] \quad (8)$$

where P_{Barge} is the cost of cargo shipment in $[\$/t]$, depending of trip duration, tow horsepower motor and payload and m_{cargo} is the annual amount of lignin shipped.

The model of lignin storage facility is based on one described by (Rentizelas et al., 2009).

The simulation has been performed in Matlab. The input data used in the techno-economic model is summarized in Table 2.

2.5.3. LCA model

By definition, LCA is a method aimed to analyze the environmental impact of a product at all stages of its life, i.e. from raw material extraction and treatment, through product processing and use, and finally to the product utilization or disposal, thus, referring to the so-called “cradle-to-grave” concept. However, sometimes, when it is necessary to focus attention on a separate product life stage, or analyze a value added process, such LCA types as “cradle-to-gate”, “gate-to-gate” and “cradle-to-cradle” can be used.

This study will utilize WTW analysis of biofuels, thus taking into account inputs/outputs from feedstock handling to vehicle tailpipe emissions. It will make use of the Greenhouse Gases, Regulated Emissions, and Energy Use in Transportation (GREET) model (version 1.3.0.12704, 2015) which has been developed at the Argonne National Laboratory.

As it was discussed in Section 2.4, there are two approaches to energy provision in cellulosic bio-refineries that in fact may be crucial for LCA. Hence, first, the two energy scenarios for bio-refineries will be modelled, one with consumption of electricity from the grid

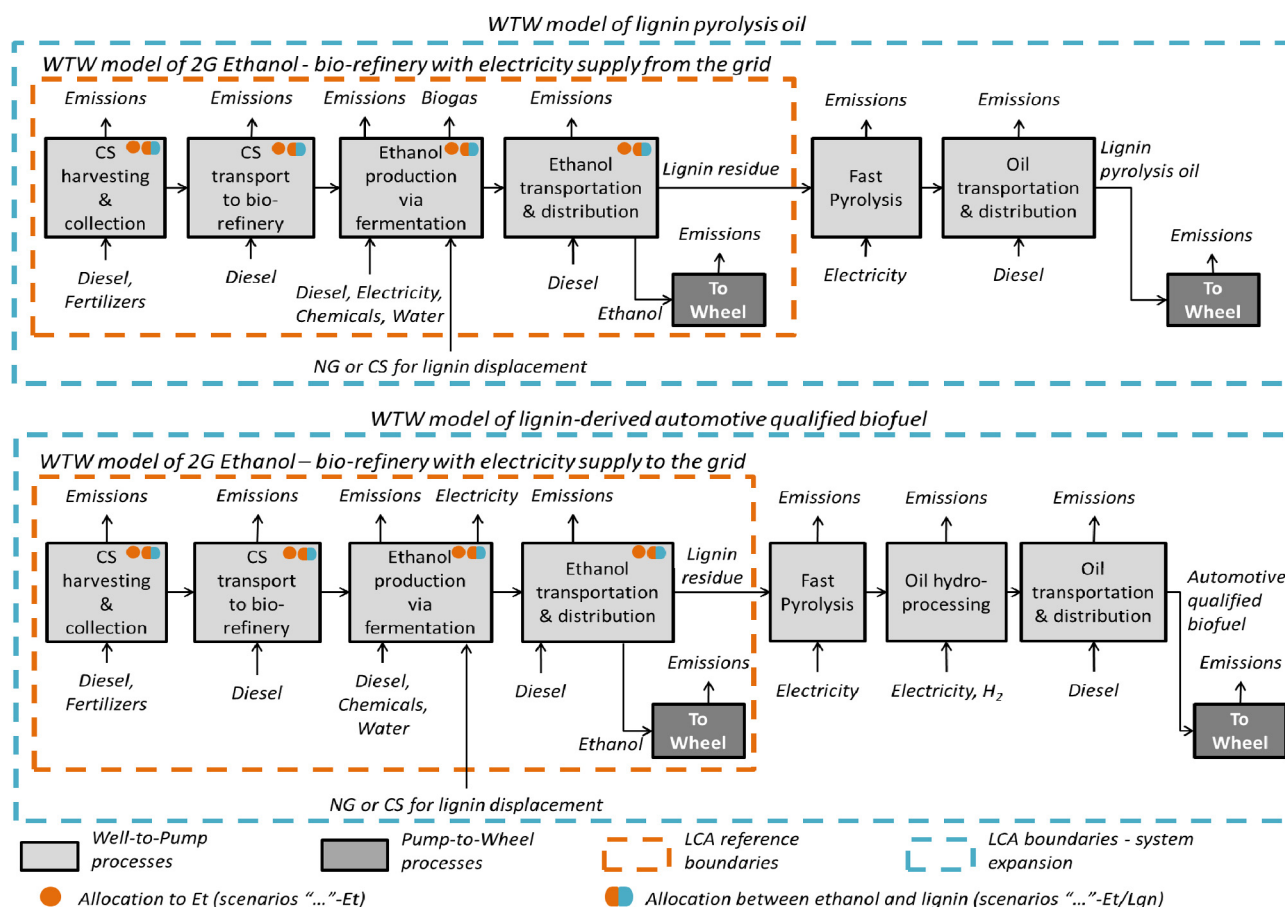


Fig. 3. LCA boundaries of biofuel pathways (NG – natural gas; CS – corn stover).

(e.g., Project Liberty) and the other with electricity production on-site (e.g., DuPont). Next, the LCA boundaries are expanded in order to accommodate aforementioned lignin-to-fuels processes (Fig. 3). Thus, while the reference system boundaries include such processes as CS harvesting and collection, feedstock transport, ethanol production, its transportation and distribution and combustion in engine, the expanded system boundaries accumulate all processes related to the reference system plus new processes, such as fast pyrolysis, hydroprocessing (for scenarios resulting in automotive qualified biofuel), biofuel transportation and distribution and its use.

In the analysis, an energy-based functional unit of 1 MJ has been selected, mainly due to necessity to analyze different types of co-products produced by a bio-refinery. Pertaining to the allocation of GHG emissions, two scenarios will be explored on an energy basis (Figs. 1 and 3), namely apportion of GHG emissions solely to ethanol in a bio-refinery and a variant whereby emissions are divided between ethanol and lignin. These two types of allocation approaches are chosen to cope with uncertainty related to such new pathway of biofuel production as lignin-to-bio-oil.

2.5.4. Lifecycle inventory data

The main input and output data used in the LCA model is summarized in Table 2.

Corn stover (CS) harvesting is associated with the removal of a part of stover remaining on the field after harvesting the corn. Since the CS is a residue stream, the emissions to be accounted for are those related only to the stover harvesting and to additional fertilizers, required to substitute chemical compounds that usually come with the stover unless it is removed (Wang et al., 2011).

Heavy heavy-duty trucks have been taken for feedstock transportation with a typical biomass loss rate of 2.0%. Additionally, the biomass moisture content default value of 12% applied by the GREET has been increased to 15%, that is in compliance with information from several sources (PNNL, 2009; USDOE, 2010). CS intake is assumed to be of 0.0036 and 0.0028 DT per liter of bioethanol produced in the year 2015 for the Project Liberty and the DuPont bio-refineries, respectively. For the POET facilities, a part of corn cobs along with separated lignin-rich stillage and sludge obtained in the anaerobic digestion system are burnt in an on-site 37 MW solid fuel boiler (ENSR/AECOM, 2008), while at the DuPont bio-refinery a part of CS and lignin are being burnt in a CHP plant for steam and electricity production. The initial data for the modelling of lignin stillage and waste water treatment (WWT) sludge are provided in Table 2.

Concerning to energy provision, while the first bio-refinery type consumes electricity from the grid (of about 1.08 kWh per liter of ethanol), the bio-refinery with electricity production generates of about 1.57 kWh per liter of ethanol, of which 0.54 kWh is assumed to be sold to the grid that will be accounted as emission credits in the model. The data of Midwest Reliability Organization has been utilized in the model in order to represent electricity mixes used by the plants. However, the first type of bio-refinery might obtain some credits for biogas production. In the model, it was assumed that an anaerobic digester produces about 0.0029 t of biogas per one liter of ethanol. The biogas composition was assumed to be 60% of CH₄ and 40% of CO₂ (POET, 2015). The produced biogas, after having been cleaned, is being fired in a boiler instead of natural gas (NG). In the model, the source of the displaced NG has been

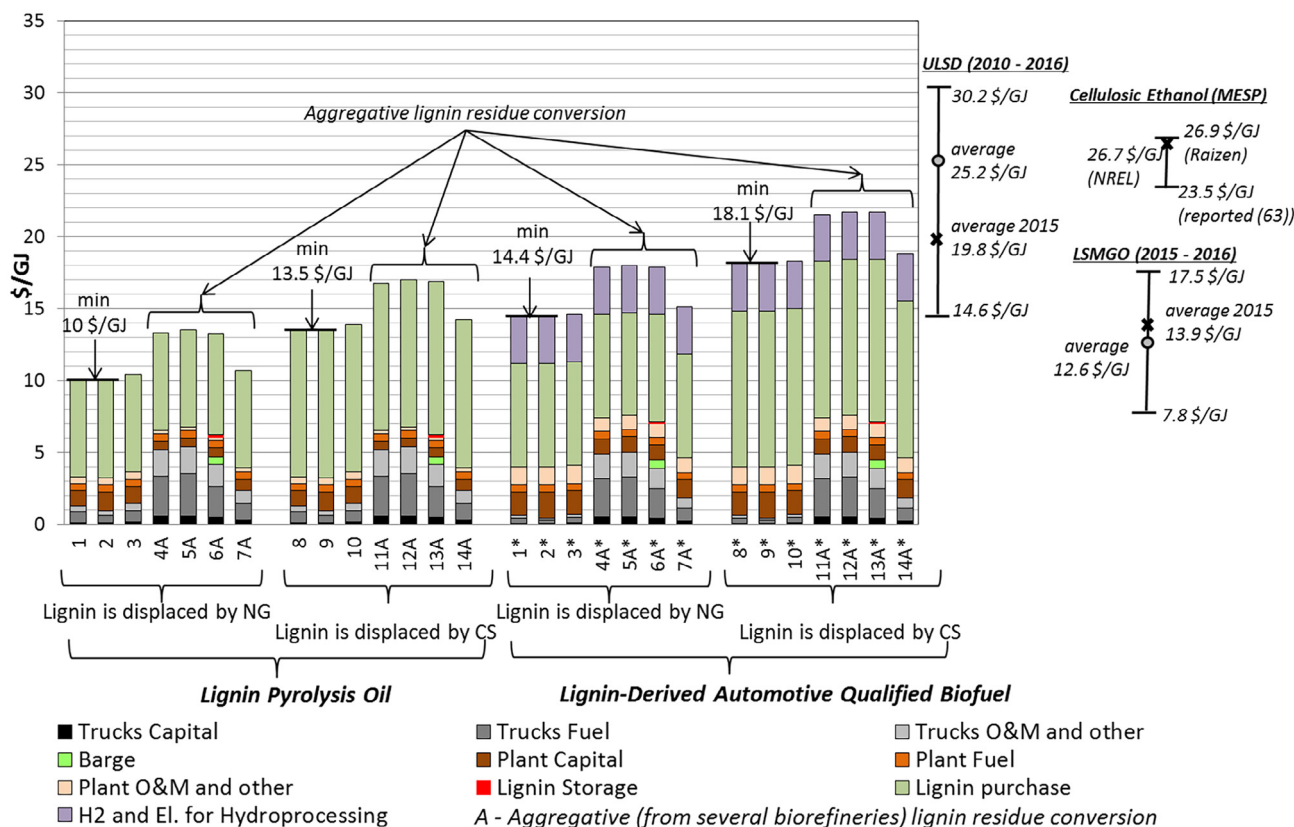


Fig. 4. Cost of bio- vs. fossil fuel production (NG – natural gas; CS – corn stover; ULSD – ultra-low sulfur (0–15 ppm) diesel; LSMGO – low sulfur (<0.1%) marine gas oil; MESF – minimum ethanol selling prices).

selected as “North America NG from shale and regular recovery as stationary fuel”.

This study utilizes the pyrolysis process with the yield of lignin pyrolysis oil (on dry basis) at the level of 33% (PNNL, 2009). The yield of automotive qualified biofuels in upgrading step amounts to 42% (Wright et al., 2010).

3. Results and discussion

3.1. Techno-economics

3.1.1. Centralized vs. decentralized

In all cases reviewed, aggregative lignin residue conversion (4A–7A, 11A–14A, 4A*–7A*, 11A*–14A* scenarios in Fig. 4) cannot compete with the decentralized approach. Minimal production and transport costs for lignin based low sulfur marine and automotive diesel vary from 10 to 13.5 and 14.4 to 18.1 \$/GJ, respectively. The discrepancy owes much to prohibitively expensive transportation costs of low energy density lignin residue. The latter, in particular, supports obtained previously results concerning the high cost of biomass transportation (Bramakis et al., 2014; Li and Hu, 2016). Another overall observation indicates that the average radius of CS collection (50–80 km) appears to be the main limitation for the treatment of lignin residue obtained from two or more biorefineries. This, in particular, can be seen from scenarios 7A, 7A*, 14A, 14A*, representing the centralized concept where lignin was collected from the two most closely located (161 km) biorefineries.

3.1.2. Truck vs. barge

In spite of considerably cheaper transportation costs in the barge option (0.6 cents/ton/km vs. 18.3 for truck one for scenarios 6A, 6A*, 13A, 13A*), given the existing logistic scheme as well as

short-term predictions for the 2G ethanol market, it appears to be impossible to compensate for detrimental economics of the aggregative lignin conversion concept.

3.1.3. Corn stover (CS) vs. natural gas (NG) as alternative energy carrier

When benchmarked against U.S. LSMGO, lignin pyrolysis oil can yield a profit from 0.4 to 3.9 \$/GJ in the event lignin residue is displaced by CS (scenarios 8, 9) and NG (scenarios 1, 2), respectively. A similar benefit can be expected from the hydroprocessed product when benchmarked against U.S. ULSD. Said benefits range from 1.7 to 5.4 \$/GJ in the event the lignin residue in question is displaced by CS (scenarios 8*, 9*) and NG (scenarios 1*, 2*), respectively.

Overall, lignin purchase cost dominates through all scenarios with the share of about 50–76% of the total annualized production cost (Fig. 4), reaching maximal values in scenarios where lignin residue in cellulosic bio-refineries is displaced by CS. The increase of lignin purchase cost to up to 10.26 \$/GJ in those scenarios is due to considerably higher cost of CS compared to NG. Obtained results are also in concordance with other studies indicating at determinative cost of biomass feedstock (Frag and Chaouki, 2015).

3.2. LCA

LCA results are summarized in Fig. 5.

Overall, LCA reveals that the choice of allocation procedure is the main determinant with respect to whether or not the lignin fuels meet the 60% well-to-wheel (WTW) GHG reduction threshold set by the U.S. renewable fuel standard (RFS), required to qualify as a second generation biofuel. Whenever GHG emissions are allocated to ethanol alone, both lignin-based low sulfur marine (scenarios 1-Et and 2-Et) and automotive diesel fuel (scenarios 1*-Et

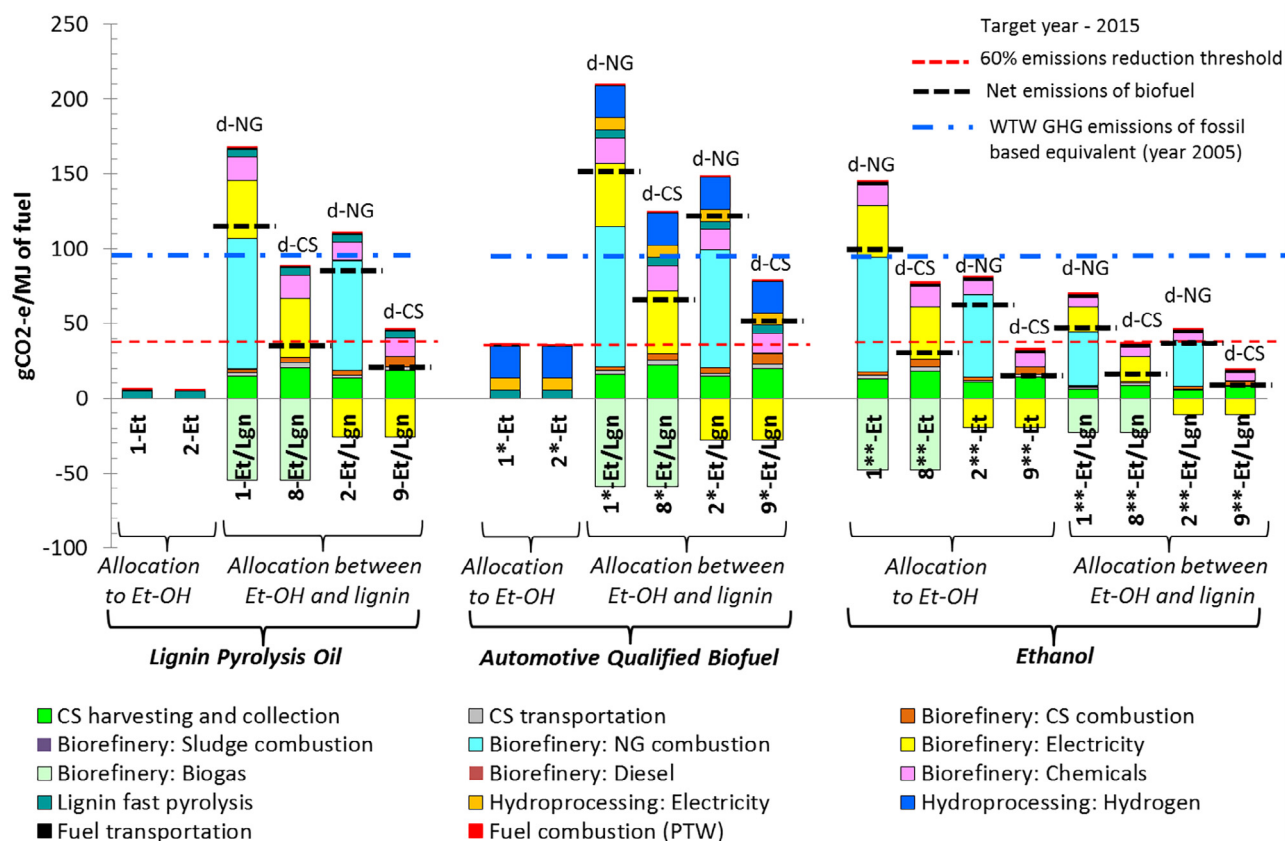


Fig. 5. WTW GHG emissions of the various fuel products from 2G ethanol plants.

and 2*-Et) comply with aforementioned threshold, bolstering reductions of 93.5–93.8% and 60.8–61.9%, respectively. WTW GHG emissions associated with ethanol, however, exceed the threshold when NG is opted for as alternative energy carrier (scenarios 1**-Et and 2**-Et).

The situation is reversed when emissions are allocated amongst both ethanol and lignin (Fig. 5). In such scenarios, automotive fuel no longer meets the 60% threshold, irrespective of alternative energy carrier. This is mainly due to emissions associated with the hydrogen and electricity required for the hydroprocessing (e.g., scenarios 1*-Et/Lgn, 2*-Et/Lgn, 8*-Et/Lgn and 9*-Et/Lgn).

In all cases whereby lignin residue is displaced by CS, lifecycle WTW GHG emissions of both lignin low sulfur marine fuel (scenarios 8-Et/Lgn and 9-Et/Lgn) and 2G ethanol (scenarios 8**-Et/Lgn and 9**-Et/Lgn) surpass the 60% threshold, yielding reduction of 64.5–78.8% and 84.2–90.2%, respectively.

Combining the techno-economic and LCA results, a critical trade-off emerges pertaining to the alternative energy carrier of choice. The use of NG over CS increases profits to 3.9 and 5.4 \$/GJ for lignin pyrolysis oil before and after hydroprocessing, respectively. Conversely, WTW GHG emissions of all fuels surge to levels no longer in compliance with the RFS.

The other obvious observation following from LCA results, but also affecting inevitably the process economics is tremendous dependence on the product (i.e. oil) yield. Since GHG emissions are accounted on per MJ basis of the final product, the oil yield of around thirty percent utilized in the current case resulted roughly in three times higher emissions assigned to e.g. bio-refinery. To this end, processes resulting in higher oil yield would be highly desirable not only from economic perspectives but also from LCA point of view. One of the potential cases that can be treated in future research is direct hydrodeoxygenation, revealing the oil yield of 64.3–67.2 wt% for solid Kraft lignin used as the feed (de Wild et al., 2017).

4. Conclusions

This paper investigated the environmental economics of fast pyrolytic conversion of lignin into two classes of biofuels, namely low sulfur marine and, by way of subsequent hydroprocessing, ultra-low sulfur automotive diesel. The results suggest that a) lignin should be processed to fuels on-site, b) the process should be limited to fast pyrolysis alone (i.e., aim for low sulfur marine fuel), and c) the choice of alternative energy carrier can make or break both the business and environmental case.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.biortech.2017.06.157>.

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